

NO_x Control & Measurement Technology for Heavy-Duty Diesel Engines Project ID: ACE032

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H. Hess, H.-Y. Chen **Johnson Matthey Inc.**

DOE Vehicle Technologies Office Annual Merit Review & Peer Evaluation Meeting June 3, 2020; Virtual Meeting due to COVID-19

ORNL is managed by UT-Battelle, LLC for the US Department of Energy

VTO Program Managers:

Gurpreet Singh, Siddiq Kahn, Ken Howden, Mike Weismiller



Overview

Timeline

- Started in 2018 VTO AOP Lab Call
 - AOI-1E: Low Temperature Emissions Control (Heavy Duty)
- Year 2 of 3-year
 - Start Date: Oct. 1, 2018
 - End Date: Sept. 30, 2021
 - Percent Complete: 53%

Budget

- 1:1 DOE: Cummins cost share
- FY20 DOE Funding: \$450k
 - DOE share: \$450k
 - Cummins share: \$450k (in kind)

Barriers

- From **21**st **CTP Research Blueprint**:
 - Emission control cost
 - Low-temperature emission control
 - Robustness in real-world application
- From **U.S. DRIVE Roadmap**:
 - Low-temperature emission control
 - Compliance via Real Driving Emissions (RDE)
 - Emissions control durability

Partners

- ORNL & Cummins Inc.
- Johnson Matthey (participant)





Milestones

FY	Qtr	Milestone & Objectives	Status
2019	4	Assembled data from protocol experiments on DeGreened commercial catalyst	complete
2020	2	Develop and tune a detailed half-cycle model	complete
2020	4	Assemble data from protocol experiments on FA commercial catalyst	on track



Responses to 2019 Review Comments

- Recommend to look at sulfur poisoning and high temperature ageing on CI
 - The field-aged sample has sulfur and hydrothermal ageing
- Include more characterization for directing project & reference ageing literature
 - − We have included additional (NH₃-TPD, DRIFTS, EPR from literature, NO+NH3 titration) characterization performed at Cummins and insights from the literature, and used these to guide model development.
 - Scheduled H₂-TPR to quantify Cu using ORNL's new Micrometrics AutoChem II 2920 reactor
- Need to consider impacts of oil poisons, EGR fouling byproducts, PGM poisons, and thermal ageing when studying field-aged samples
 - Cummins has provided a representative field-aged sample
 - Project will focus on the critical application-relevant Hydrothermal and Sulfur aging components
- Recommend to include a sensor and catalyst supplier
 - Sensor insights are procured through Cummins' in-kind contributions
 - Johnson Matthey is a project participant
- Need more modeling resources
 - Saurabh and Rohil are leading multiple coordinated modeling teams focused on the CRADA objectives





Collaborations and Coordination

- ORNL: Bill Partridge (ORNL PI)
- Cummins: Saurabh Joshi (Cummins PI)
- Johnson Matthey: Howard Hess (JM Lead)
 - Formally included in CRADA and Project documentation



Teamwork & Roles

Johnson Matthey ORNL Cummins Diagnostics Model catalyst Modeling Measurements samples Field ageing **Joint** Planning · Results interpretation Monthly+ telecons



- Interactions with technical community
 - 5 Presentations (3 invited)
 - 1 Technical report









Key Challenge Addressed by Project

- Improving *Durability* of urea-SCR catalysts in Heavy Duty engine applications
- Project focuses on understanding *Field-Ageing* process and impacts
 - Impact on SCR reaction network & kinetic parameters
 - Improved models
 - Improved design & control models
 - Improved durability through better SCR through-life performance
 - Methods for synthetic field ageing
 - Hydrothermal ageing does not represent field ageing
 - Improve catalyst performance & durability under Real-World Driving Conditions



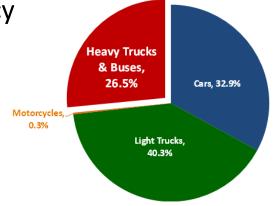
Relevance

 Improved Field-Ageing Models & Understanding critical to meeting increasing performance requirements

Heavy Heavy-Duty Emissions Regulations					
Current	Proposed '27	Proposed '31			
CARB/EPA	CARB	CARB			
Useful Life (miles,hr)	Useful Life (miles,hr)	Useful Life (miles,hr)			
435,000 (10yr, 22k hr)	600,000 (11yr, 30k hr)	800,000 (12yr, 40k hr)			

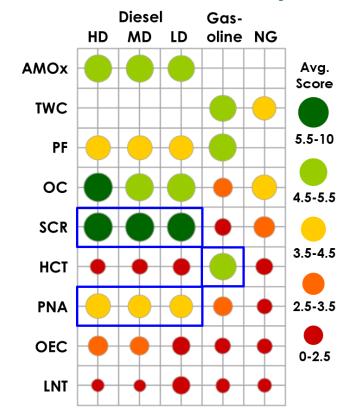
Rapidly Increasing Warranty & Useful-Life Demands

 Better catalyst performance allows engine to be optimized for fuel efficiency



On-Highway Petroleum Use (Source: Transportation Energy Data Book)

2019 CLEERS Industry Priorities Survey



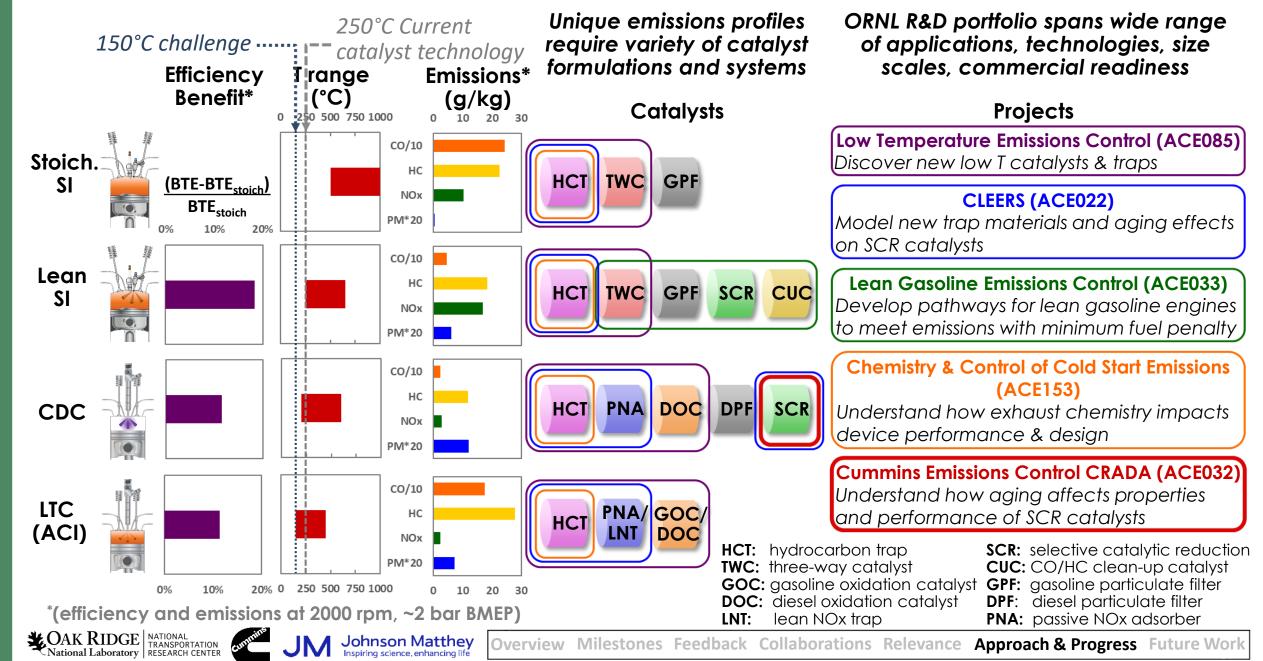
- SCR top technology for Diesel
- SCR Aging: #3 for all HDD tech. & topics



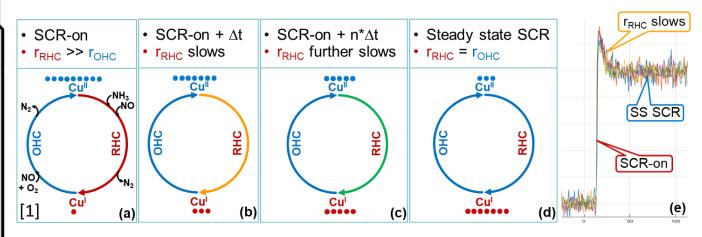




Low Temp. Emissions-Control Challenges Affect Multiple Platforms



Background: Determine Kinetic Impacts of Field Ageing via Transient-Response Cu-Redox Half-Cycle Analysis

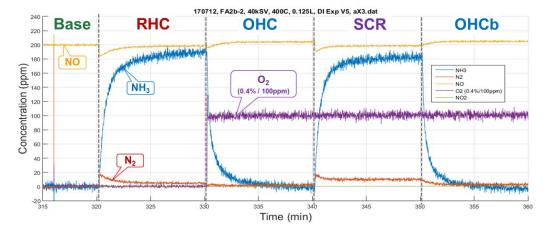




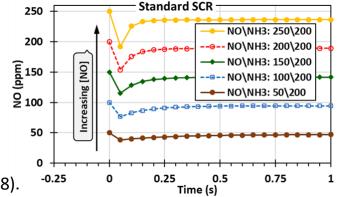
- RHC: Reduction Half Cycle oxidized Cu (Cu^{II}) is reduced to Cu^I
- OHC: Oxidation Half Cycle $Cu^{I} \rightarrow Cu^{II}$ completing the cycle
- Cl occurs when the RHC rate > OHC rate
- CI shape reflects on half-cycle kinetic parameters

Use transient analysis to study SCR Field-Ageing

- Kinetic impact on individual RHC & OHC
- Insights: ageing process, better lab ageing, models, ...



- Transient Cu-Redox Experimental Protocol
 - Individual & combined half cycles
- Simple Kinetic Model developed
 - Reproduces experimental CI trends



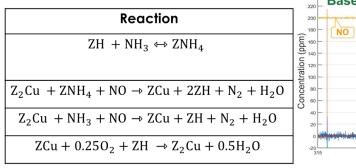
[1] Partridge et al., Appl. Catl. B, V236, p195(2018).

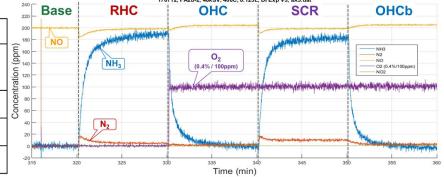






- 1. Use Transient-Response Method to determine SCR kinetic parameters
 - 1.a Measure CI transient shapes
 - 5-Step Redox Protocol & spatiotemporal mapping
 - 1.b Develop Cu-redox model





	DeGr	DeGreened HT-Aged		Field	Aged	Cu ^{II} (NH ₃		
	RHC	OHC	RHC	OHC	RHC	OHC	N ₂	
E _a							SH SH	
Α							NO) + O ₂ Cu ¹ (a)	

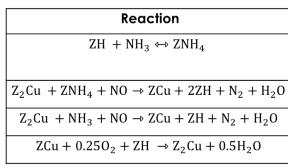
SCR Channel

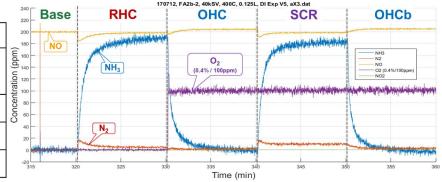






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 - **1.a** Measure CI transient shapes
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 - **1.b** Develop Cu-redox model
 - **1.c** Fit RHC & OHC kinetic parameters
 - Using data & Cu-redox model





	DeGr	eened	HT-Aged		Field	Aged	Cu ^{II} (NH ₃		
	RHC	OHC	RHC	OHC	RHC	OHC	N ₂		
E _a			6.5E9	1.5E6			SE S		
A			70	30			NO) + O ₂ Cu ¹ (a)		

SCR Channel

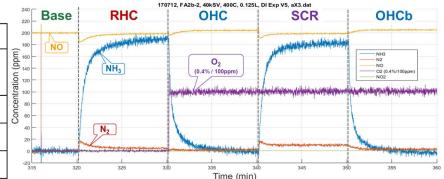






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Reaction
$ZH + NH_3 \leftrightarrow ZNH_4$
$\boxed{ Z_2Cu + ZNH_4 + NO \rightarrow ZCu + 2ZH + N_2 + H_2O }$
$Z_2Cu + NH_3 + NO \rightarrow ZCu + ZH + N_2 + H_2O$
$ZCu + 0.25O_2 + ZH \rightarrow Z_2Cu + 0.5H_2O$



- 2. Baseline DeGreened catalyst kinetic parameters
 - Steps 1.a & 1.b

	DeGreened		HT-Aged		Field	Aged	Cu ^{II} NH ₃ NO
	RHC	OHC	RHC	OHC	RHC	OHC	N ₂
Eα	FY20	FY20	6.5E9	1.5E6			OHO OHO
Α	FY20	FY20	70	30			NO) + O ₂ Cu ¹ (a)

SCR Channel

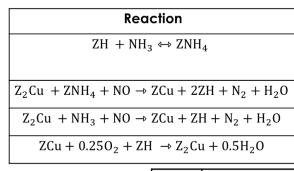
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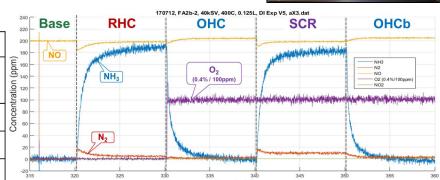




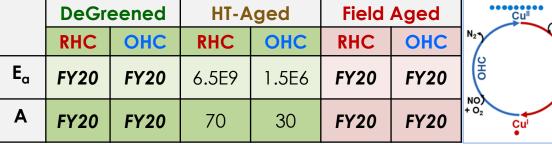


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- 2. Baseline DeGreened catalyst kinetic parameters
 - Steps 1.a & 1.b
- **3.** Study how *Field Ageing* impacts kinetic parameters
 - RHC & OHC kinetic impacts vs. DeG values
 - Pathways to improved durability and control
- **4.** Study how Catalyst *Formulation* impacts kinetic parameters
 - Mechanistic origin of formulation benefits
 - Pathways to improved low-temperature aged performance



SCR Channel

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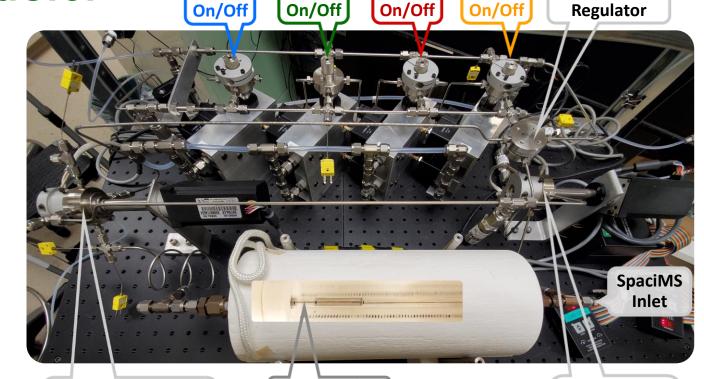






Transient-Response Reactor

- MicroReactor scale:
 - ca. 1LPM total flow
 - ca. 8-mm Dia x 25-mm Long cores
 - Separate Powder-Bed leg
- Multiple flow switching:
 - H20
 - E.g., O_2 , NO_y , NH_3 (or other)
- Designed for transient studies
 - Heated switching valves
 - Minimum dead-end runs
 - Minimized flow paths/volumes
- Programmable unattended operation
 - Greater throughput
- Instrumentation
 - SpaciMS for intra-catalyst
 - FTIR outlet & inlet (via Bypass)



Leg combiner

- Selected to FTIR
- Others to Vent

Catalyst Core



Powder

Leg Selector

Back-Pressure

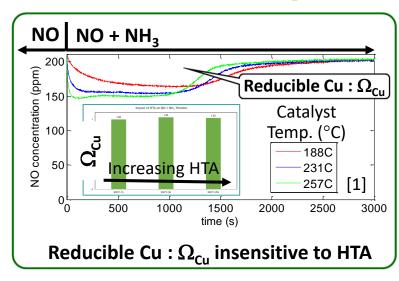
Bypass

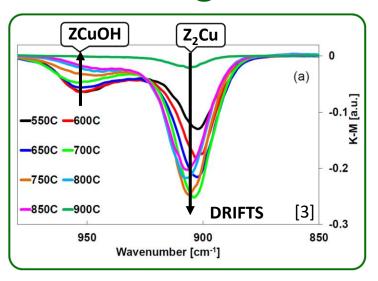


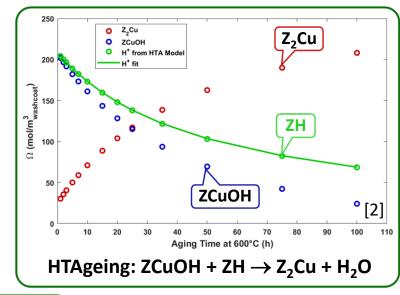




Model Assumptions from HT-Aged Catalyst Characterization



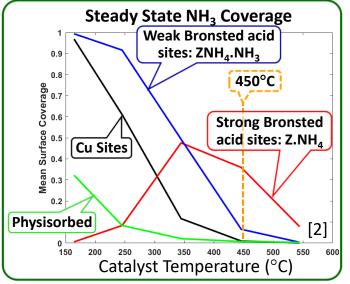




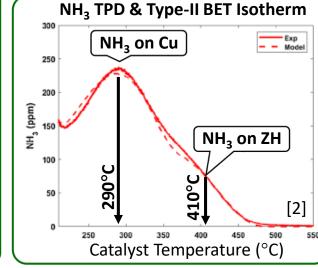
(Hydrothermally Aged Cu-SSZ-13 catalyst)

Modeling assumptions & inputs follow:

- Ω_{Cu} from NO+NH₃ titration
 - Insensitive to HTA
- Z₂Cu is primary reducible Cu site after HTA
- $\Omega_{\rm ZH}$ from NH₃ TPD
- NH₃ stored only on Strong ZH sites ≥450°C
- Two RHC pathways considered at ≥450°C
 - Surface (θ_{ZNH4}) and gas-phase (y_{NH3}) NH₃







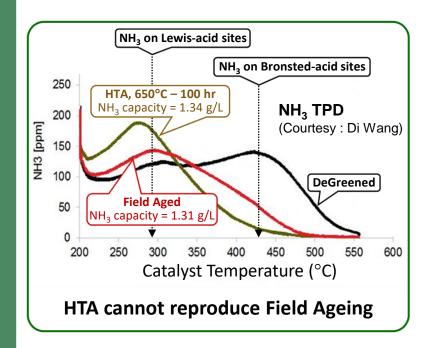
- [2] Daya et al., Appl. Catl. B, V263, p118368 (2020).
- [3] Luo et al., SAE 2015-01-1022.

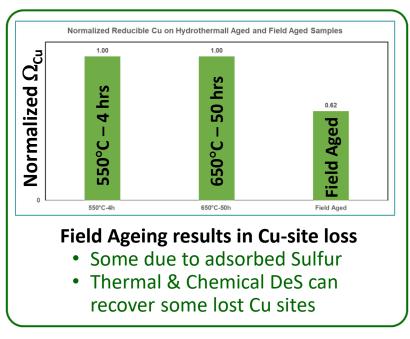


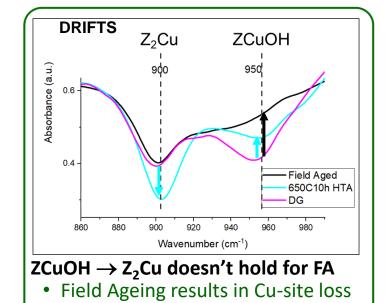




Field-Ageing is Different from Hydrothermal Lab Ageing







Both ZCuOH & Z₂Cu generally lower

- Field Ageing is complex
 - Many components contributions
 - can be difficult to separate
 - Not replicated by controlled lab ageing
- Many are studying Lab Ageing
 - Advancing imperfect understanding
 - Many details yet to be understood

- Practical value in studying Field Ageing
 - More relevant than Hydrothermal Ageing
 - Properties can be characterized
 - Use to reject 'atypical' field-aged samples
 - Determine impacts on kinetic parameters
 - Understand and untangle component ageing contributions
 - Insights for improved Modeling & Lab Ageing



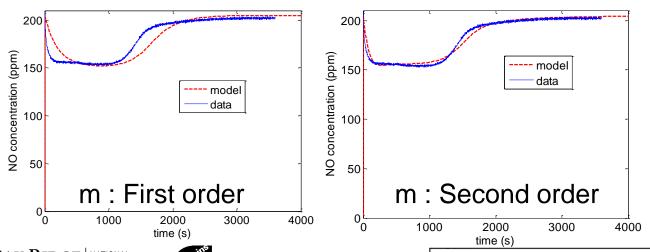




RHC Global-Kinetic Model

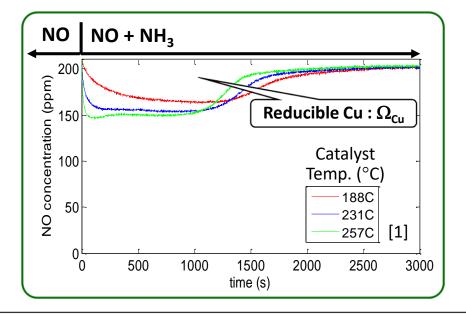
$NH_3 + S \leftrightarrow NH_3 - S$	$R_1 = k_{f1} C_{NH3} (1 - \theta_{NH3}) - k_{b1} \theta_{NH3}$	←	NH ₃ adsorption & desorption
$Cu^{II}+NO+NH_3 \rightarrow Cu^I+N_2+2H_2O$	$R_2 = k_{RHC} \theta_{Cu}^m \theta_{NH3} C_{NO}^n$	+	RHC

- RHC kinetic parameters from RHC-step experiments
 - NO+NH₃ titration (zero O₂) at three temperatures
 - $-\Omega_{Cu}$ from NO conversion
 - Ea and m from fitting
 - Initial NO consumption rate increase with temperature
- Parameters from experimental data; e.g. θ_{Cu}^m :



Global lumped parameters

- θ_{Cu} : Fractional Reducible-Cu sites
- θ_{NH3} : Fractional NH₃ coverage
- Ω_{NH3} : NH₃ site density
- Ω_{Cu} : reducible Cu site density

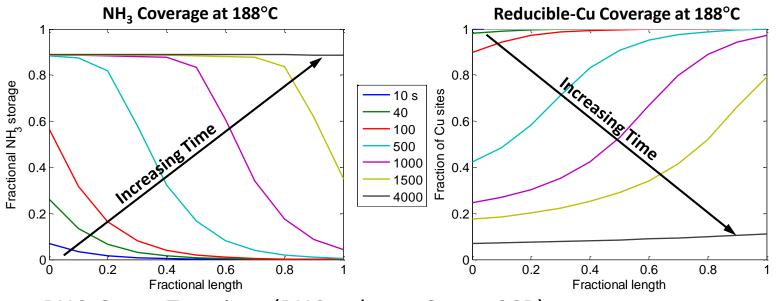


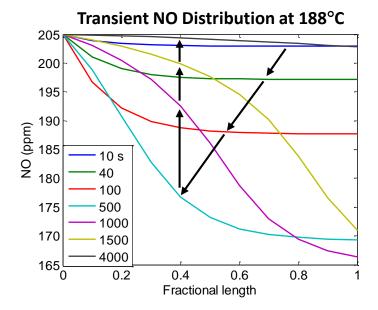




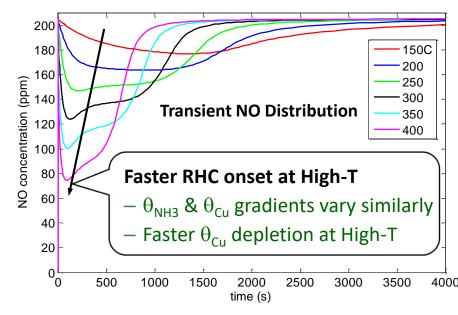


Spatiotemporal Progression of RHC (using global NH₃ ads/desorption model)





- RHC-Onset Transient (RHC only, no O₂, no SCR)
 - θ_{NH3} builds as θ_{Cu} is depleted
 - Causes NO conversion profile to grow and decay
 - Creates a slow onset transients at Low-T & faster at High-T
 - Fast, step-like onset transients at \geq 250°C (for case here)
- Influences SCR-onset CI due to RHC-OHC rate imbalances
 - Little imbalance with slow RHC onset at Low-T \rightarrow no CI
 - Pronounced imbalance with faster RHC onset \rightarrow CI grows with T
 - Consistent with FY19 work: CI threshold & CI grows with T







Kinetic SCR Model Formulation & Redox Parameter Fitting

Reaction	Rate Expression	
$ZH + NH_3 \leftrightarrow ZNH_4$	$r_{NH_3Ads_{ZH}} = k_{NH_3Ads_{ZH}} y_{NH_3} \theta_{ZH} \Omega_{ZH} $	│ ├─ NH₃ adsorption & desorptio
	$r_{NH_3Des_{ZH}} = k_{NH_3Des_{ZH}} \theta_{ZNH_4} \Omega_{ZH}$	
$Z_2Cu + ZNH_4 + NO \rightarrow ZCu + 2ZH + N_2 + H_2O$	$r_{RHC1_{Z_2Cu}} = k_{RHC1_{Z_2Cu}} y_{NO} \theta_{Z_2Cu} \theta_{ZNH_4} \Omega_{Cu} \leftarrow$	RHC1 - Adsorbed NH ₃
$Z_2Cu + NH_3 + NO \rightarrow ZCu + ZH + N_2 + H_2O$	$r_{RHC2_{Z_2Cu}} = k_{RHC2_{Z_2Cu}} y_{NO} y_{NH_3} \theta_{Z_2Cu} \Omega_{Cu} \leftarrow$	– RHC2 – NH₃ gas
$ZCu + 0.25O_2 + ZH \rightarrow Z_2Cu + 0.5H_2O$	$r_{OHC1_{ZCu}} = k_{OHC1_{ZCu}} y_{O_2}^{0.25} \theta_{ZCu} \theta_{ZH} \theta_{ZCu} \Omega_{Cu} \leftarrow$	OHC OHC

- Modeled in AVL BOOST
- Developed for HT-Aged Commercial Cu-SSZ-13 catalyst at ≥450°C
 - Other reactions at Lower-Temp; e.g. NH₃ storage on Cu sites
 - Low-Temp RHC example uses global NH₃ ads/desorption; a lumped site

OHC

- Several parameters in [1 & 2]
 - NH₃ ad/desorption, Ω_{Cu} , Ω_{7H}
- Redox params fitting
 - Effluent SCR-on CI transient
 - CI is weakest at L=1
 - Expect better fits with CI at catalyst front

Redox Killetic Paralleters						
Parai	neter	Value		Unit		
DUC1	Α	3.75E+11		1/s		
RHC1	Ea	70	[3]	kJ / mol		
RHC2	Α	6.53E+09		1/s		
KHC2	Ea	70	[3]	kJ / mol		

1.5E+06

30

Podov Kinotic Parameters

- Ω_{Cu} : Number density, Reducible-Cu sites
- ZH: Bronsted-acid sites
- Ω_{7H} : Number density, ZH
- ZNH₄: strongly adsorbed NH₃
- Z₂Cu: primary reducible Cu site after HTA
- ZCu : reduced Cu
- NH_3 stored only on ZH sites $\geq 450^{\circ}C$
- Two RHC pathways considered
- [1] Daya et al., Appl. Catl. B, V263, p118368 (2020).
- [2] Luo et al., J. Catal., V3448, p291-299 (2017).
- [3] Paloucci et al., J. ACS, 138(18), 6028-6048 (2016).



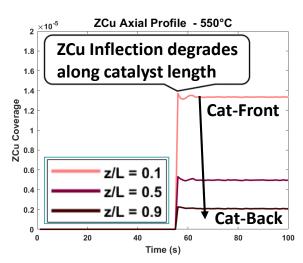


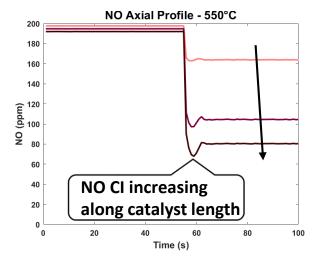


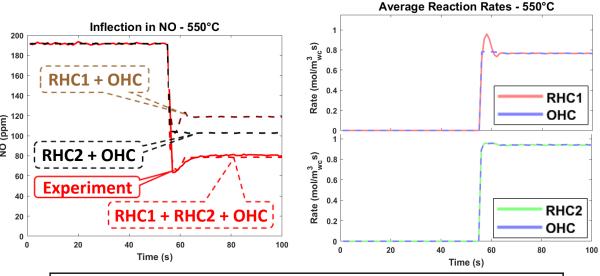
1/s

kJ / mol

SCR-Onset Transient







- Experiments show CI degrades along catalyst
 - ZCu inflection follows this trend, but NO CI does not
- Model allows turning different reactions on & off
 - RHC1+OHC shows onset CI, while RHC2+OHC does not
 - OHC rate is equal or faster than RHC1 & RHC2
 - Will not produce onset RHC-OHC balancing and CI
 - Suggests OHC rate is too fast
- Multiple solutions for the Redox Kinetic Parameters
 - Need more extensive SpaciMS database for fitting
 - More distinct CI at catalyst front should help fit

- **Redox Kinetic Parameters Parameter** Fit-1 Value Fit-2 Value Unit 3.75E+113.75E+11 1/s RHC1 Ea 70 70 kJ / mol 6.53E+09 6.53E+09 1/s RHC2 Ea kJ / mol 70 1.5E+06 3.26E+07 1/s OHC Ea kJ / mol 30 50
- Kinetic model demonstrated & exercised
- ZCu inflection trends follow Exp. observations
- Method for fitting kinetic params demonstrated
- SpaciMS database should provide better results



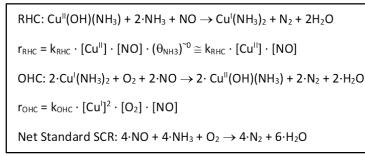


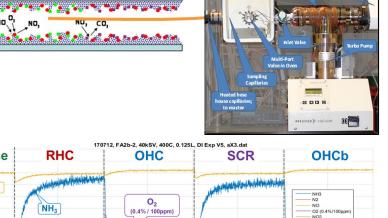


1.a Measure CI transient shapes

1. Use Transient-Response Method to determine SCR kinetic parameters

- - 5-Step Redox Protocol & spatiotemporal mapping
 - **1.b** Develop Cu-redox model





					Time (min)	l.		
	DeGreened		ned HT-Aged		Field	Aged	Cu ^{II} (NH ₃	
	RHC	OHC	RHC	OHC	RHC	OHC	N ₂	
Ea							SH SH	
A							NO) + O ₂ Cu ¹ (a)	

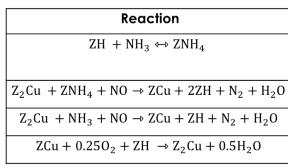
SCR Channel

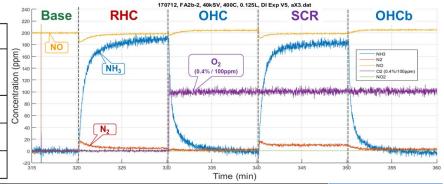
RHC





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	DeGr	eened	HT-A	ged	Field	Aged	Cu ^{II} CNH ₃	
	RHC	OHC	RHC	OHC	RHC	OHC	N ₂	
E _a			6.5E9	1.5E6			SE S	
Α			70	30			NO) + O ₂ Cu ¹ (a)	

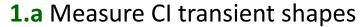
SCR Channel





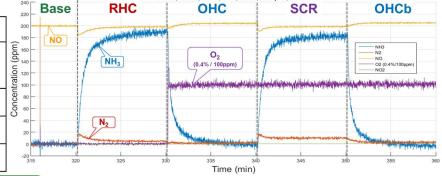


1. Use Transient-Response Method to determine SCR kinetic parameters



- 5-Step Redox Protocol & spatiotemporal mapping
- **1.b** Develop Cu-redox model
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 - Using data & Cu-redox model

Reaction
711 + 1111 4 5 7 1111
$ZH + NH_3 \leftrightarrow ZNH_4$
7 (7NII NO 7(27II N II O
$Z_2Cu + ZNH_4 + NO \rightarrow ZCu + 2ZH + N_2 + H_2O$
$Z_2Cu + NH_3 + NO \rightarrow ZCu + ZH + N_2 + H_2O$
2200 11113 110 200 211 1120
$ZCu + 0.25O_2 + ZH \rightarrow Z_2Cu + 0.5H_2O$

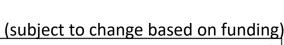


- 2. Baseline DeGreened catalyst kinetic parameters
 - Steps 1.a & 1.b

		Processes Name (
	DeGreened		HT-Aged		Field Aged		Cu ^{II} ⟨NH₃
	RHC	OHC	RHC	OHC	RHC	OHC	N ₂
Eα	FY20	FY20	6.5E9	1.5E6			원 왕
Α	FY20	FY20	70	30			NO) + O ₂ Cu ¹ (a)

SCR Channel

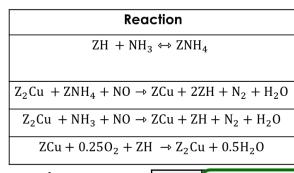


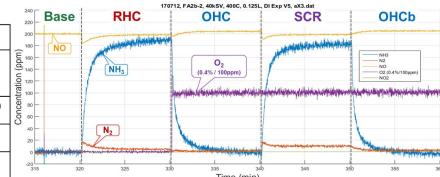






- 1. Use Transient-Response Method to determine SCR kinetic parameters
 - **1.a** Measure CI transient shapes
 - 5-Step Redox Protocol & spatiotemporal mapping
 - **1.b** Develop Cu-redox model
 - **1.c** Fit RHC & OHC kinetic parameters
 - Using data & Cu-redox model





- 2. Baseline DeGreened catalyst kinetic parameters
 - Steps 1.a & 1.b
- **3.** Study how *Field Ageing* impacts kinetic parameters
 - RHC & OHC kinetic impacts vs. DeG values
 - Pathways to improved durability and control
- **4.** Study how Catalyst *Formulation* impacts kinetic parameters
 - Mechanistic origin of formulation benefits
 - Pathways to improved low-temperature aged performance



SCR Channel

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(subject to change based on funding)







Remaining Challenges:	Future Work: (subject to change based on funding)
-----------------------	---------------------------------------------------

Availability of transient reactor

- Complete reactor build, characterization, & commissioning
- Develop automated control



Remaining Challenges:

Future Work: (subject to change based on funding)

Availability of transient reactor

- Complete reactor build, characterization, & commissioning
- Develop automated control

Kinetic impact of Field Ageing



400 01 110101 71801118						
	DeGr	eened	Field Aged			
	RHC OHC		RHC	OHC		
Ea	FY20	FY20	FY20	FY20		
Α	FY20	FY20	FY20	FY20		

- SpaciMS with 5-Step Redox Protocol experiments
- Fit RHC & OHC kinetic parameters using kinetic model
- Assess parameter changes vs. DeGreened catalyst



Remaining Challenges:

Future Work: (subject to change based on funding)

Availability of transient reactor

- Complete reactor build, characterization, & commissioning
- Develop automated control

Kinetic impact of Field Ageing



	DeGr	eened	Field Aged	
	RHC	OHC	RHC	OHC
E _a	FY20	FY20	FY20	FY20
Α	FY20	FY20	FY20	FY20

- SpaciMS with 5-Step Redox Protocol experiments
- Fit RHC & OHC kinetic parameters using kinetic model
- Assess parameter changes vs. DeGreened catalyst
- **Kinetic origins of improved performance** with Low-Temperature formulations
- Implement Transient Response Methodology
 - **Experimental Protocol & Model Fitting**







Remaining Challenges:

Future Work: (subject to change based on funding)

Availability of transient reactor

- Complete reactor build, characterization, & commissioning
- Develop automated control

Kinetic impact of Field Ageing



	DeGr	eened	Field Aged	
	RHC OHC		RHC	OHC
Ea	FY20	FY20	FY20	FY20
Α	FY20	FY20	FY20	FY20

- SpaciMS with 5-Step Redox Protocol experiments
- Fit RHC & OHC kinetic parameters using kinetic model
- Assess parameter changes vs. DeGreened catalyst
- Kinetic origins of improved performance with Low-Temperature formulations
- Implement Transient Response Methodology
 - **Experimental Protocol & Model Fitting**



Improved SCR Real-World Durability

Heavy Duty Emissions Regulations					
Current Projected '26/'2					
CARB/EPA	CARB				
Useful Life (miles)	Useful Life (miles)				
435,000 1,200,000					
Solution Pathway					

- Integrate knowledge and results
 - Improved field-ageing models
 - Improved experimental characterization methods
 - Methods for synthetic/lab field ageing
 - Methods for catalyst-state assessments
 - Tools for improved design, control and diagnosing





Summary

Relevance

- Focus is on kinetic origin of low-temperature performance and field aged SCR catalysts
- Project work enables improved catalyst knowledge, models, design, OBD & control
- Advances DOE goals for improved fuel economy, durability, & real-world emissions

Approach

- Apply experimental protocol to probe transient response of Cu-redox half-cycle steps
- Develop and apply model to fit Cu-redox half-cycle kinetic parameters
- Study kinetic impacts of low-temperature formulations and field-aged catalysts

Technical Accomplishments

- Built Transient Reactor developed for 5-Step Redox Protocol data
- Developed Detailed RHC-OHC redox model
- Demonstrated method for fitting RHC & OHC kinetic parameters

Collaborations

- Johnson Matthey incorporated as project and CRADA participant
- Communicate with community via presentations & publications
- Future Work (Any proposed future work is subject to change based on funding levels)
 - Determine impact of field-ageing on kinetics of commercial Cu-SSZ-13 SCR catalyst
 - Determine kinetic origins of performance for low-temperature formulations



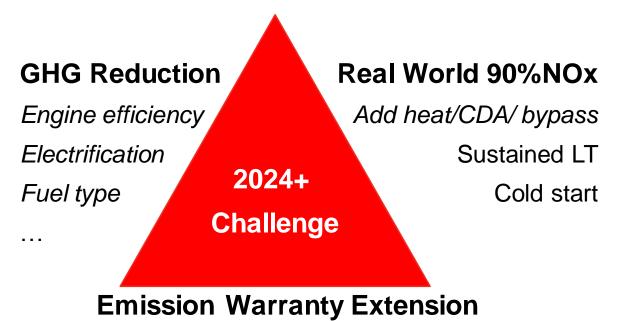


Technical Back-Up Slides



Motivation – Tailpipe NO_x and Durability Requirements

Future Application Challenges



Class	2022	2027 (forecast)
HD	5Y 350K miles	14Y 800K miles
MD	5Y 150K miles	14Y 400K miles

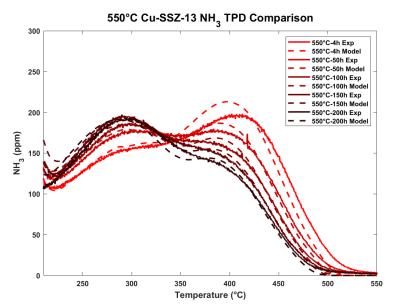
Overall approach to meet these challenges includes

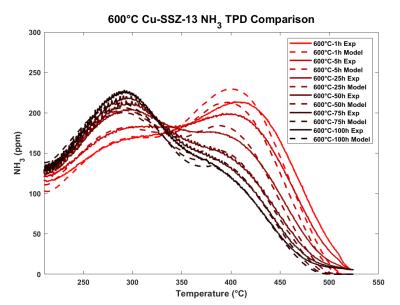
- a) Adaptable Controls
- b) Improved understanding and modeling of real world aging
- c) Improved Component durability (higher resistance to real world aging)

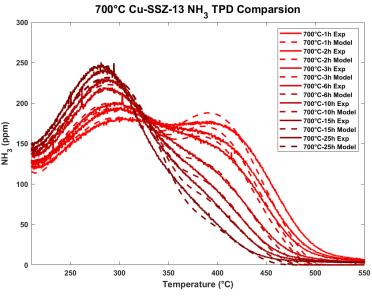


Modeling the change in NH₃-TPD with hydrothermal aging

- NH₃-TPD experiments indicate a monotonic decrease in high temperature peak and increase in low temperature peak with increased aging
- This behavior was modeled with:
- a) Fixed turnover rates (identified previously)
- b) Increased NH₃ storage ability on Copper sites with aging
- c) Decreased number density of Brønsted acid sites with aging



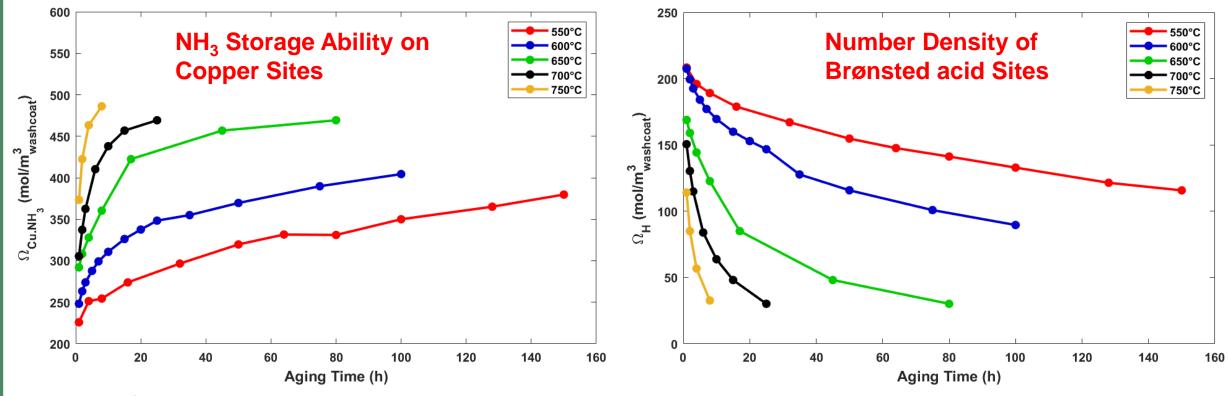




OAK RIDGE NATIONAL Luo, J., Gao, F., Kamasamudram, K., Currier, N., Peden, C. H., & Yezerets, A. (2017). New insights into Cu/SSZ-13 SCR catalyst acidity. Part I: Nature of acidic sites probed by NH 3 titration. Journal of Catalysis, 348, 291-299.

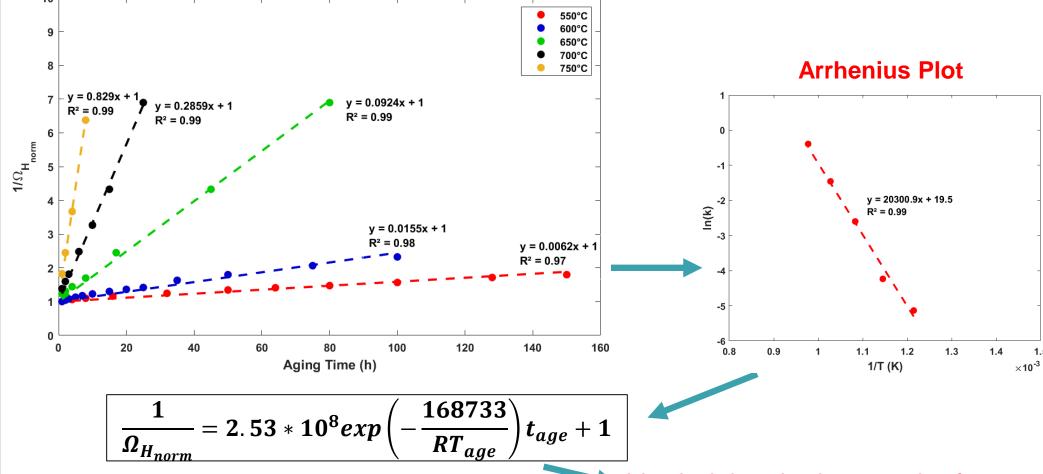
Tracking Storage Capacity on Copper Sites and Number Density of Brønsted Acid Sites

- Increase in NH₃ storage on copper sites is linearly related to the loss of Brønsted acid sites
- The loss of Brønsted acid sites with aging is used to develop a constitutive relationship for the evolution of these sites, yielding the hydrothermal aging equation



Hydrothermal Aging Equation

 A linear relationship is found between the inverse Brønsted acid site density and aging time, implying a second order Arrhenius rate. The rate constant and activation energy are derived

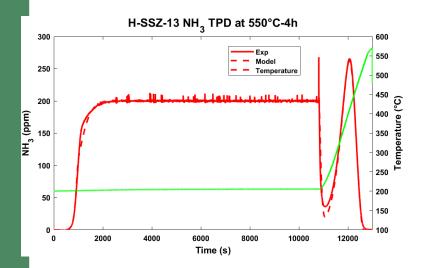


Ratio-based calculator reported previously

 $\text{Nation} \frac{1}{r} = 3.4 \times 10^8 \exp\left(-\frac{168000}{RT}\right) * t + 0.938$

Identical deactivation energies from two different derivation methods

Impact of HTA on Brønsted Acid Sites



Cu-SSZ-13 NH₃ TPD at 750°C-4h

Cu-SSZ-13 NH₃ TPD at 750°C-4h

Exp

Model
Temperature

- 350

- 450

- 400

- 350

- 300

- 250

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Cu-SSZ-13 NH₃ TPD data at 750°C-4h

600°C Cu-SSZ-13 NH₃ TPD Comparison

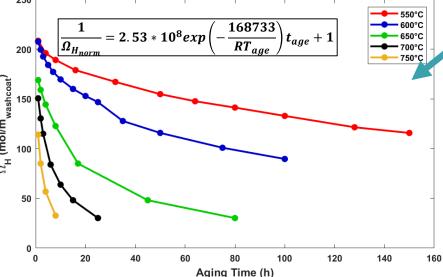
550°C-750°C TPD data gives site number densities for fixed storage turnover rates

H-SSZ-13 NH₃ TPD data gives Brønsted acid site storage kinetics

Adsorption Thermodynamics for NH₃ Storage on Individual Active Sites

Adsorption Thermodynamics for 14113 Storage on Marvadan Active Sites					
Reaction	K_{eq} at	$\Delta_{ads}H^0(kJ/mol)$	$\Delta_{ads}S^{0}(J/mol-K)$		
	200°C				
$NH_3 + ZH \Leftrightarrow Z.NH_4$	8.08e+08	$-134 (\alpha = 0.11)$	-113		
$NH_3 + Z.NH_4 \iff Z.NH_4.NH_3$	2.19e+05	-63	-31		
$NH_3 + Cu \Leftrightarrow Cu. NH_3$	3.11e+04	$-103 \ (\alpha = 0.11)$	-111		
$NH_3 + P \Leftrightarrow P.NH_3$	1.06e+03	-38	-23		

Luo, J., Gao, F., Kamasamudram, K., Currier, N., Peden, C. H., & Yezerets, & A. (2017). New insights into Cu/SSZ-13 SCR catalyst acidity. Part I: Nature of acidic sites probed by NH 3 titration. *Journal of Catalysis*, 348, 291-299. Daya, R., Joshi, S. Y., Luo, J., Dadi, R. K., Currier, N. W., & Yezerets, A. (2020). On kinetic modeling of change in active sites upon hydrothermal aging of Cu-SSZ-13. *Applied Catalysis B: Environmental*, 263, 118368.



gives Copper site kinetics

Brønsted acid site density correlated with aging time and temperature via an Arrhenius equation

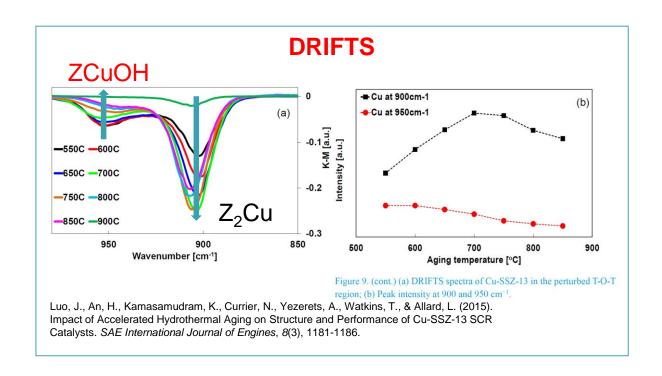
Experimental Data: Jinyong Luo

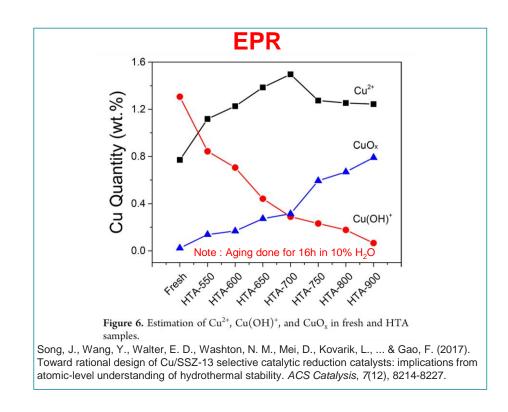


Impact of HTA on Copper Sites

DRFITS and EPR estimated Cu site quantification shows:

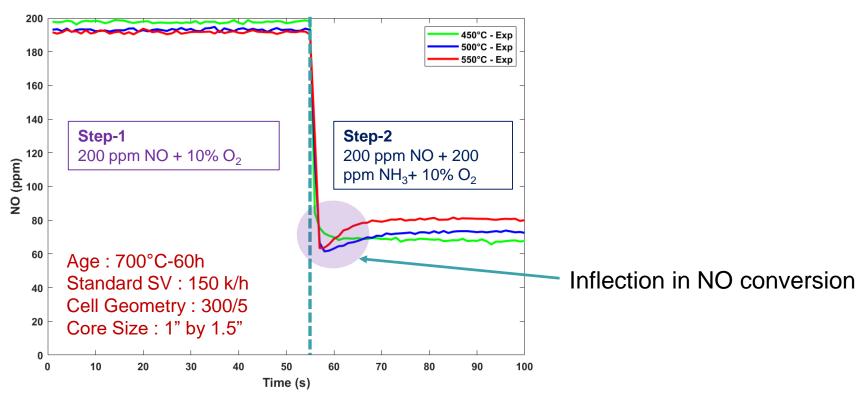
- a) Monotonic decrease in number of ZCuOH sites with increased HTA temperature
- b) Increase in number of Z₂Cu sites with increased HTA temperature up to 750°C
- c) Decrease in number of Z_2 Cu sites upon severe HTA at an aging temperature $\geq 750^{\circ}$ C
- d) Increase in number of CuO_x sites upon severe HTA at an aging temperature ≥ 750°C





Experimental Evidence for Conversion Inflection on Aged Cu-SSZ-13

Commercial Cu-SSZ-13 catalyst shows conversion inflection at the onset of SCR during step-2 of the 4-step protocol [5] at high SV for temperatures ≥ 500°C

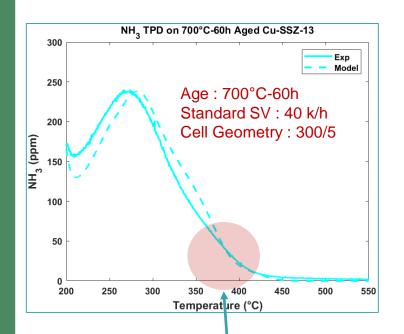


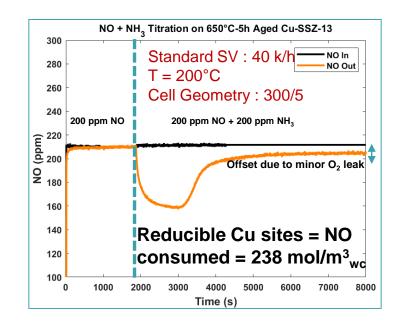
[5] Kamasamudram, K., Currier, N. W., Chen, X., & Yezerets, A. (2010). Overview of the practically important behaviors of zeolite-based urea-SCR catalysts, using compact experimental protocol. *Catalysis Today*, 151(3-4), 212-222.

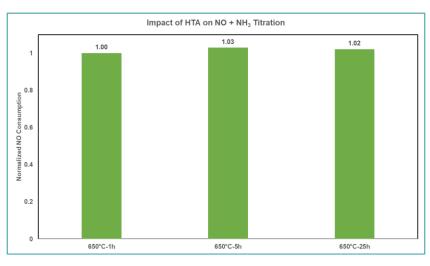


Kinetic Model Parameters – Site Densities

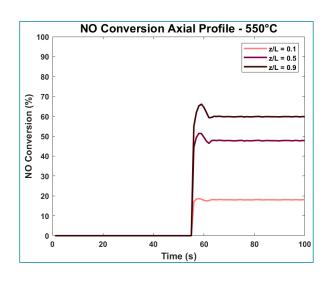
- The kinetics for NH₃ storage on Bronsted acid sites were the same as the published results in [2]
- The number density of Bronsted acid sites ($\Omega_{\rm ZH} = 8.91~{\rm mol/m^3_{wc}}$) in the oxidized catalyst was identified based on the minor high temperature NH₃ release peak during TPD experiments [2]
- The number density of reducible Copper sites was estimated from NO+NH₃ titration experiments on a degreened catalyst ($\Omega_{\text{Cu}} = 238 \text{ mol/m}^3_{\text{wc}}$). It has been shown that is value is insensitive to hydrothermal age, and therefore the same value was used for the 700°C-60h aged catalyst

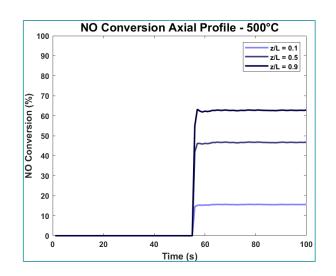


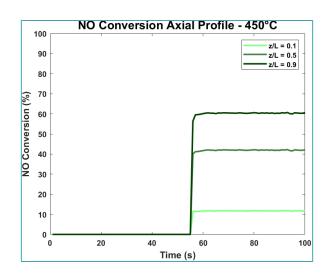


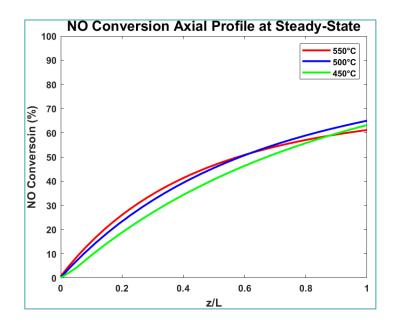


Model Results – NO Conversion Axial Profile



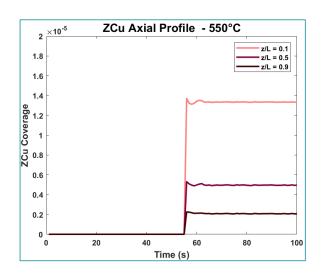


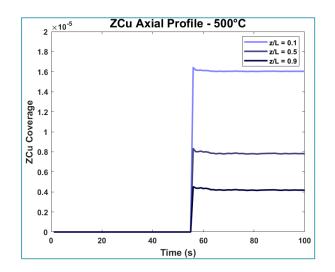


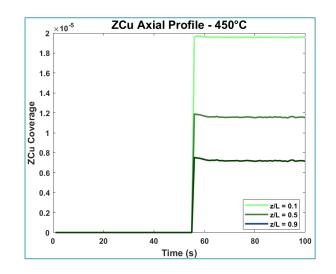


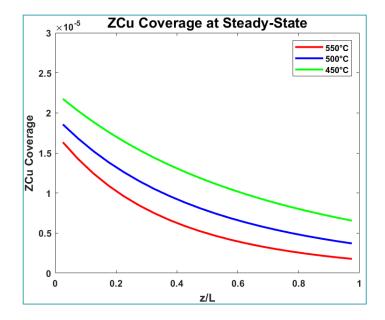
As expected, NO conversion profiles are essentially mirror images of the outlet NO concentration profiles

Model Results – ZCu Axial Profile



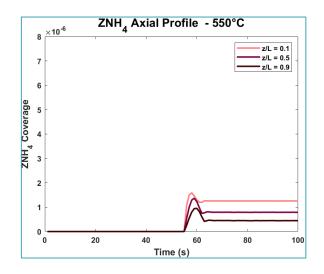


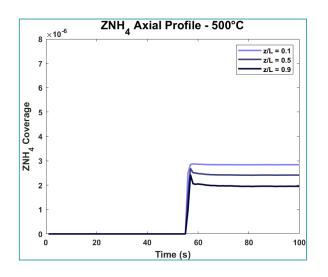


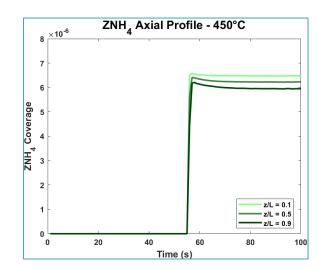


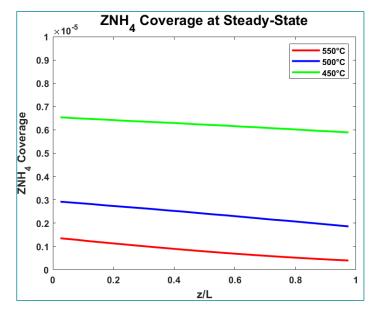
- Minor inflection in ZCu coverage observed due to imbalance in RHC and OHC rates
- ZCu coverage decreases along the length of the SCR catalyst at all temperatures, due to decrease in NH₃ coverage and partial pressure
- ZCu coverage decreases with increase in SCR temperature, due to increase in oxidation half cycle rate, and desorption of NH₃

Model Results – ZNH₄ Axial Profile







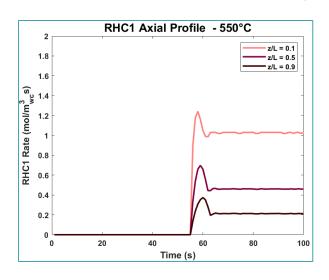


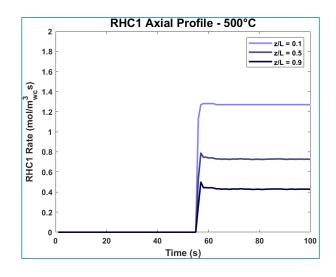
- ZNH₄ coverage at 550°C goes through a maximum before reaching steady-state, due to competition between adsorption and RHC1
- This inflection in ZNH₄ coverage leads to an inflection in NO consumption
- ZNH₄ coverage decreases with increase in catalyst temperature due to desorption of NH₃

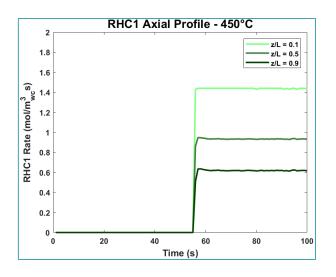


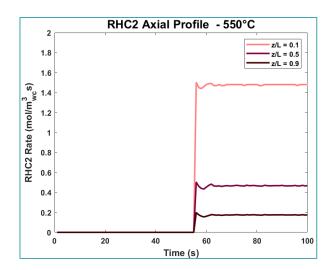
Model Results – RHC Axial Profile

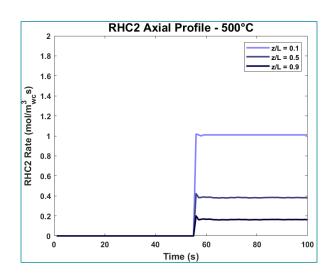
Inflection in RHC caused by ZNH₄ coverage, while minor inflection in RHC2 associated with ZCu coverage

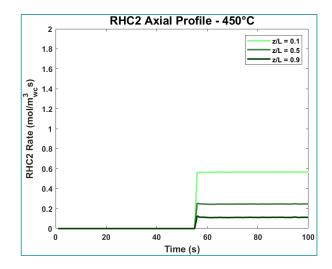






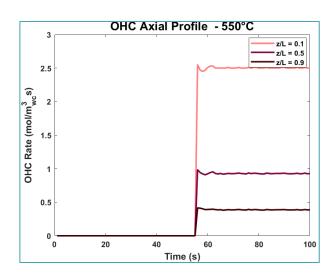


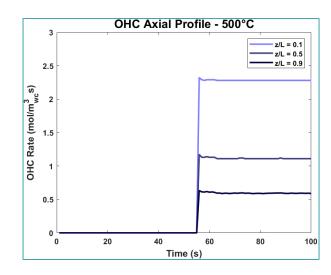


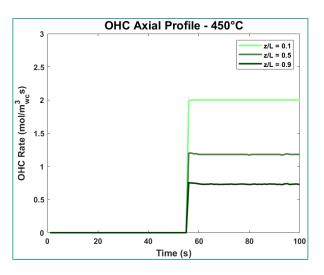


Model Results – OHC Axial Profile

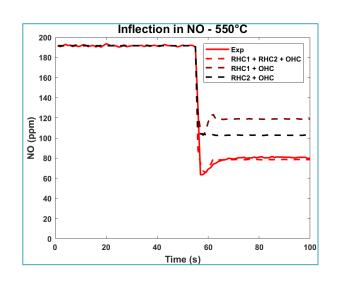
- OHC rate decreases along the length of the catalyst, due to drop in ZCu coverage axially
- Minor inflection at onset of SCR observed in OHC at 550°C due to the maximum in ZCu coverage associated with imbalance of RHC and OHC rates

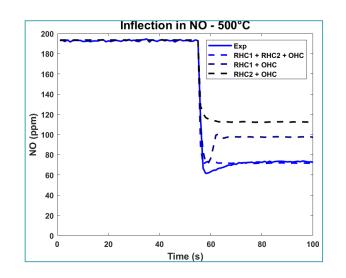


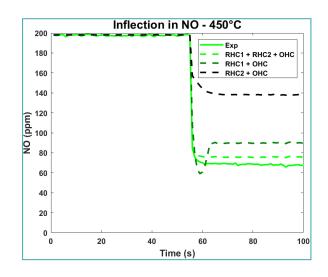




Model Results – Influence of Individual RHC Reactions







- Kinetic model was simulated with turning off RHC2 (RHC1 + OHC only) and turning off RHC1 (RHC2 + OHC only)
- Interestingly, the inflection observed with RHC1 + OHC is significant at all temperatures. The influence of RHC2 appears to dampen this inflection, such that the combined model only shows this behavior at the highest temperature (550°C)